1 Properties of waves

1.1 Waves

Consider a periodic wave traveling with velocity v and wavelength λ.[1] The following quantities are defined in terms of v and λ:

- Time between peaks: $T = \lambda/v$, $\quad [T]$ = s.

- Frequency: $\nu = \frac{1}{T} = \frac{v}{\lambda}$, $\quad [\nu]$ = s^{-1}.

- Angular frequency: $\omega = 2\pi\nu$, $\quad [\omega]$ = rad s^{-1}.

In empty space light travels at the speed of light (a constant), $c = 299792458 \text{ m s}^{-1}$. For light then wavelength and frequency are related by:

$$\lambda\nu = c. \tag{1}$$

1.2 Blackbody radiation

According to classical physics, an idealized blackbody at temperature T emits radiation with a given energy density $\rho(\nu, T)$, where ν is the frequency of the light emitted. The quantity $\rho(\nu, T)d\nu$ is the total energy emitted per unit volume in the range of frequencies $[\nu, \nu + d\nu]$ and is given by the expression

$$\rho(\nu, T)_{\text{Classical}}d\nu = \frac{8\pi k_B T}{c^3}\nu^2 d\nu \quad [\text{J} \times \text{m}^{-3}] \tag{2}$$

where k_B is the Boltzmann constant

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}\text{particle}^{-1}. \tag{3}$$

Exercise 1.1 Draw a plot of $\rho(\nu, T)_{\text{Classical}}$ for two temperatures, T_1 and T_2 with $T_1 < T_2$. ∎

Exercise 1.2 The total energy emitted by a blackbody is given by the integral over all emitted frequencies, that is, the integral over ν from 0 to infinity of $\rho(\nu, T)_{\text{Classical}}$. Evaluate this integral.

$$\int_0^\infty \rho(\nu, T)_{\text{Classical}}d\nu = \frac{8\pi k_B T}{c^3}\int_0^\infty \nu^2 d\nu = \frac{8\pi k_B T}{c^3}\left.\frac{\nu^3}{3}\right|_0^\infty = \infty! \tag{4}$$

∎

The divergence of the integral that determines the total energy emitted is known as the **ultraviolet catastrophe** because it is due to the incorrect behavior of $\rho(\nu, T)_{\text{Classical}}$ for large frequencies. The solution to this problem came from Max Planck (1900). Planck assumed that light could be describe as a set of harmonic oscillators, and that each oscillator carried only a discrete amount of energy:

$$E = nh\nu, \tag{5}$$

where $n = 0, 1, 2, \ldots$ is a positive integer and h is Planck's constant

$$h = 6.626070040(81)10^{-34} \text{ J s}. \tag{6}$$

Using this assumption Planck derived the following equation

$$\rho(\nu, T)_{\text{Planck}} = \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}, \tag{7}$$

which shows the correct behavior.

Exercise 1.3 What is the value of $\rho(\nu, T)_{\text{Planck}}$ for $\nu = 0$? Expand $\rho(\nu, T)_{\text{Planck}}$ as a Taylor series in the variable ν centered around $\nu = 0$. Does this equation agree with the classical expression $\rho(\nu, T)_{\text{Classical}}$? ∎

1.3 The photoelectric effect

The photoelectric effect, discovered by Heinrich Hertz (1887), consists in the production of electric sparks when a metal is illuminated with ultraviolet light. Experimentally, one finds that the kinetic energy (K) of the electrons emitted is given by

$$K = \begin{cases} 0 & \text{if } h\nu - \Phi \leq 0 \\ h\nu - \Phi & \text{if } h\nu - \Phi > 0, \end{cases} \tag{8}$$

where Φ is called the work function and depends on the metal and h is Planck's constant. The work function is the amount of energy required to remove an electron from the metal and create a free electron with zero kinetic energy. This result disagrees with a classical interpretation of the experiment, in which one assumes that the kinetic energy is proportional to the intensity of the light used in the experiment.

Albert Einstein was able to explain the photoelectric effect by assuming that a photon of frequency ν carries an energy equal to

$$E = h\nu, \tag{9}$$

and that each photon can produce only one electron. Using the relationship between frequency and wavelength we also can express the energy of a photon as

$$E = h\frac{c}{\lambda}. \tag{10}$$

1.4 Units and conversion factors

Spectroscopist use a variety of units to report energy differences. The wave number ($\tilde{\nu}$) is defined as the number of waves per unit length

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{E}{hc}. \tag{11}$$

so that in SI units it is measured in m^{-1}. However, it is more convenient to express wave number in units of cm^{-1}, which is done by multiplying by 0.01. Here are some conversion factors to remember:

$$1\,\text{kcal/mol} = 349.75\,\text{cm}^{-1}\,\text{molecule}^{-1}, \tag{12}$$

and

$$1\,\text{cm}^{-1}\,\text{molecule}^{-1} = 29\,979.2458\,\text{MHz}. \tag{13}$$

Another useful energy unit is electron volt (eV)

$$1\,\text{eV} = (\text{charge of } e^-)(1\text{V}) = 1.602 \times 10^{-19}\,\underbrace{CV}_{J} = 8065.54\,\text{cm}^{-1}. \tag{14}$$

1.5 Time scales for molecular motion

Regions of the electromagnetic spectrum with the corresponding molecular transitions are reported in Table 1.

Table 1: Regions of the Electromagnetic Spectrum

Region	Wavelength	Wave number	Frequency	Molecular process
Microwave	0.04–25 cm	0.04–25 cm^{-1}	1.2–750 GHz	Molecular rotations
Infrared	2.5–25 μm	400–4000 cm^{-1}	1.2×10^{13}–1.2×10^{14} Hz	Fundamental vibrations
Visible	400–800 nm	12500–25000 cm^{-1}	3.7×10^{14}–7.5×10^{14} Hz	Valence electronic excitations
Near ultraviolet	10–200 nm	25000–50000 cm^{-1}	7.5×10^{14}–1.5×10^{15} Hz	Valence electronic excitations
X-rays	1–10 Å	10^7–10^8 cm^{-1}	3×10^{17}–3×10^{18} Hz	Ionization of inner shell electrons

We can estimate time scales (τ) for different molecular process from the inverse of the frequency of the light causing a transition

$$\tau = \frac{1}{\nu} = \frac{\lambda}{c} = \frac{1}{\tilde{\nu}c} = \frac{1}{(\tilde{\nu}\,\mathrm{cm}^{-1}) \times (2.99 \times 10^{10}\mathrm{cm\,s}^{-1})} \tag{15}$$

Rotations

$$\tilde{\nu} = 1\,\mathrm{cm}^{-1} \Rightarrow \tau_{\mathrm{rot}} = 3.3 \times 10^{-11}\mathrm{s}^{-1} = 33\,\mathrm{ps} \tag{16}$$

Vibrations

$$\tilde{\nu} = 2000\,\mathrm{cm}^{-1} \Rightarrow \tau_{\mathrm{vib}} = 1.7 \times 10^{-14}\mathrm{s}^{-1} = 17\,\mathrm{fs} \tag{17}$$

Electronic orbits

$$\tilde{\nu} = 40\,000\,\mathrm{cm}^{-1} \Rightarrow \tau_{\mathrm{el}} = 8.3 \times 10^{-16}\mathrm{s}^{-1} = 830\,\mathrm{as} \tag{18}$$